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Synthesis of Novel Vanadium Oxide Nanotubes and Nanofibers

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ABSTRACT

We are exploring the synthesis and properties of structured vanadium oxides mainly nanotubes and nanorods. Nanotubes initially formed with surfactant templates have been readily exchanged with simple cations without change of the basal-plane structure. These compounds contain δ-like vanadium oxide layers with the vanadium in VO_6 octahedra. This structure is particularly suitable for redox reactions. In this paper we report on synthesis of vanadium oxide, $(NH_4)_xV_2O_{5-\delta}\cdot nH_2O$ rods using organic polymer as template. This compound has been synthesized by sol-gel reaction and subsequent hydrothermal treatment. TGA, SEM, XRD and FTIR were used to characterize this compound. Thermal analysis of this compound shows that the fibrous morphology is maintained when it is heated in nitrogen and oxygen above 300 °C. However, in both cases the size of the fibers decreases. Performance of this compound as cathode material in secondary electrolyte has been investigated using $LiPF_6$ as electrolyte. A capacity of 140 mAh/g was obtained which remained fairly constant with up to at least 10 cycles. We also investigated electrochemical behavior of thermal products.

INTRODUCTION

There has been much recent interest in preparing new vanadium oxides owing to their promise as cathodes and anodes in secondary lithium batteries and electrochromic devices [1-2]. Also the catalytic behavior of vanadium oxides make these materials viable candidates as heterogeneous catalysts [3]. The physical and chemical properties of substances might well be altered when they are prepared on a nanoscopic scale and thus this phenomenon opens up a completely new perspective for material design that benefits from the introduction of particle size as a new, powerful parameter [4]. Thus fabrication of vanadium oxides in nanostructured form and with anisotropic morphology appears to be a particularly attractive goal.

The first successful approach to make a tubular vanadium oxide was use of carbon nanotubes as a template [5]; it was found possible to coat crystalline layers of V_2O_5-structures on the external surfaces of the carbon nanotubes. Recently, new type of vanadium oxide nanotubes was obtained by a soft-chemistry synthesis involving amines with long alkyl chains as molecular, structure directing template [6]. This material consisted of scrolls of vanadium oxide layers within which the alkyl amines were embedded. The structure of the double-sheet layer in this material is similar to $BaV_7O_{16}\cdot nH_2O$ [7]. In our attempts to make structured vanadium oxides, we have developed a new method to make novel vanadium oxide tubes and nanorods using an organic polymer as template. The synthetic approach involved sol-gel and hydrothermal techniques. This method allows us to

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form one-dimenional materials or thin films metal oxide materials. This paper reports on the syntheses, characterization and electrochemical behavior of these novel vanadium oxide nanostructures.

EXPERIMENTAL DETAILS

Polylactide (PLA) is a biodegradable polymer derivered from renewable resources. It can be synthesized from either a condensation polymerization of lactic acid or ring opening polymerization of lactide, a cyclic dimmer of lactic acid [8]. Polylactide fibers were prepared here by an electro-spun technique using literature method [9]. The fibers used in this experiment were on average about 700 nm in diameter.

A piece of polylactide fiber about 2 cm × 2 cm was placed into 50 ml of 1M-ammonium vanadate solution. The pH of the solution was then adjusted to 3.4 using glacial acetic acid. The resulting mixture was transferred to a 125-ml Teflon–lined autoclave (Parr Bomb), sealed, and reacted hydrothermally for 3 days at 160 °C. A golden yellow solid formed which was washed with distilled water to remove acetic acid and any undecomposed products. Heating the hydrothermal product in nitrogen and oxygen resulted in the formation of $V_2O_{4.8}$ and V_2O_5 nanofibers respectively.

X-ray diffraction was performed using CuKα radiation on a Scintag θ-θ diffractometer. The FTIR data was obtained on a Perkin-Elmer 1500 series spectrometer. The morphology and the structure of the nanotubes were investigated by using XRD and SEM. Thermal stability of the fiber was investigated using TGA in oxygen and nitrogen.

The performance of these compounds as positive electrode was tested by galvanostatic cycling in the potential range 2.0-4.2 V vs Li/Li^+. In all cases the cathode consisted of about 80% sample, 10% carbon black, and 10% Teflon™.The carbon black was used to make the sample conductive since the samples of interest were not good electronic conductors. The Teflon™ was used as a binding agent to keep the pellet intact during the experiments. The cathode material was then hot pressed onto a stainless steel Exmet™ grid at 110 °C to dehydrate the sample. A metallic lithium sheet served as both the counter and reference electrode. A 1M solution of $LiPF_6$ in a 1:1 ethylene carbonate (EC) /1,2-dimethylcarbonate was used as electrolyte.

DISCUSSION

The role of the polylactide as template was confirmed from two control experiments. In one experiment 50 ml of 1M ammonium vanadate solution acidified with acetic acid to a pH of 3.4 was treated hydrothermally at 160 °C for 3 days and the product was crystalline $NH_4V_3O_8$. In the second control experiment, PLA fiber was placed in 50 ml of acetic acid solution at a pH of 3.4; then the mixture treated as above. In this case the fiber was found to have dissolved forming a colorless solution after hydrothermal treatment. The diameter of the vanadium oxide formed after hydrothermal treatment was smaller than that of the initial template suggesting that the product is formed by growing within the fiber and not by coating around it.

Thermo gravimetric analysis

This study showed the absence of the template in the hydrothermal product for two reasons namely; one, the TGA profile of the product remained the same after it was washed in a DMF/

CH_2Cl_2 mixture, which easily dissolves the template. Secondly, thermograph of the hydrothermal product was similar to that of δ-like V_2O_5 synthesized in our group. Thermo gravimetric analysis of hydrothermal product showed that it was possible to maintain the fibrous morphology by heating it in nitrogen and oxygen at 250 °C and 350 °C respectively. Figure 1 shows the thermographs of the hydrothermal product in oxygen and nitrogen.

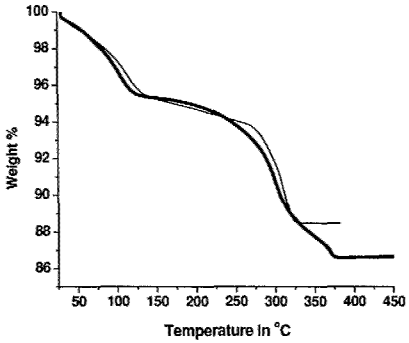

Figure 1. TGA of the hydrothermal product under nitrogen (light line) and oxygen (thick line).

Fourier transformed infrared spectroscopy

FTIR confirmed the absence of the PLA template in the hydrothermal product as the characteristic peaks for C=O at 1754 and C-H at 1392 and 1183 cm^{-1} of the template were not seen in the spectrum of the final product. Both the hydrothermal product and the vanadium oxides formed by heating it in oxygen and nitrogen showed characteristic V-O vibrations peaks between 1021 cm^{-1} and 500 cm^{-1}. Some FTIR spectra are shown in figure 2 below.

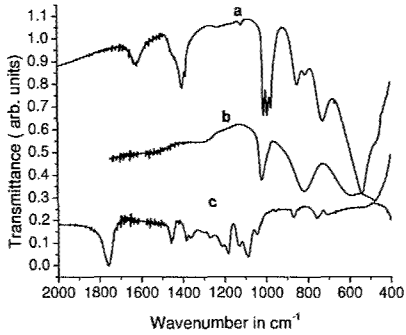

Figure 2. FTIR spectra of a) hydrothermal product, b) heated hydrothermal product in nitrogen and c) polylactide fiber.

X-ray diffraction

X-ray diffraction pattern of the hydrothermal product showed that its structure is similar to that of a δ-V_2O_5 recently made in our group [10] .The cell parameter of this compound shows similarity with other δ-V_2O_5 phases [11-12]. X-ray also confirmed that heating of the hydrothermal product in oxygen results in the formation of pure V_2O_5 nanofibers. Thus on heating in oxygen the structure changes from the double sheet of the δ-phase to the single sheet typical of V_2O_5 itself. X-ray diffraction pattern of compound formed by heating the hydrothermal product was poorly resolved and showed that it was predominantly VO_2.

Scanning electron microscopy

SEM shows that the hydrothermal product consists of fibers with the outer diameter ranging from 150-200 nm, while their lengths vary from 500 nm to a maximum of 16 μm. Closer examination of this material reveals smaller particles deposited on the surface (Figure 3a). The average diameter of the starting polylactide fibers is 700 nm, which is larger than that of the final product. This supports our earlier proposal that the product grows somehow inside the template

The SEM of the product obtained by heating the hydrothermal product in oxygen shows ribbon-like morphology and randomly orientation. The fibers exhibit a wide range of lengths and widths. Their diameters vary between 30 and 140 nm. SEM micrographs show only the presence of vanadium oxide. In some regions, fibers are curved and tangled together forming bundles. The SEM micrographs further show that the tips of these fibers are round. The SEM image of the hydrothermal product after heating in nitrogen (see figure 3 left) was investigated and typical image of the compound represented a general view of the fibrous morphology. Interestingly, the diameters of this material are longer on average than the one heated in oxygen. In some regions it appears that the fibers might be open ended. The SEM also confirmed that it is possible to heat the hydrothermal product in oxygen and nitrogen to at least 500 °C and still preserve the fibrous morphology. X-ray diffraction however shows that the fibers convert to single sheet V_2O_5 after heating in oxygen.

Figure 3. Typical SEM images of hydrothermal product (left) showing the fibrous morphology, after heating in nitrogen (middle) and V_2O_5 nanofibers (right) (product of heating the hydrothermal product in oxygen).

Electrochemistry

The cell performance of vanadium oxide fibers was investigated at a current density of 0.1 mA/cm^2 using as electrolyte $LiPF_6$ dissolved in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC); pure lithium metal was used as the counter and reference electrode. The electrochemical behavior of the hydrothermal product is shown in Figure 4. Its cycling is good with an average discharge profile around 2.0 volts and little capacity loss after multiple lithium insertions and removal. The XRD pattern of the compound after electrochemistry indicated that the structure had changed from the double sheet of the δ-phase to the single sheet of V_2O_5. Low angle peaks disappeared showing that the d spacing of the compound was reduced after electrochemistry. Probably large ions like water and /or ammonium are replaced by smaller lithium ions. The electrochemical behavior of the hydrothermal product heated in nitrogen (figure not shown) was also investigated. The compound was also electrochemically active and had a capacity of about 120 mAh/g, which remained fairly constant through 10 cycles. The compound did not change structure during these reactions.

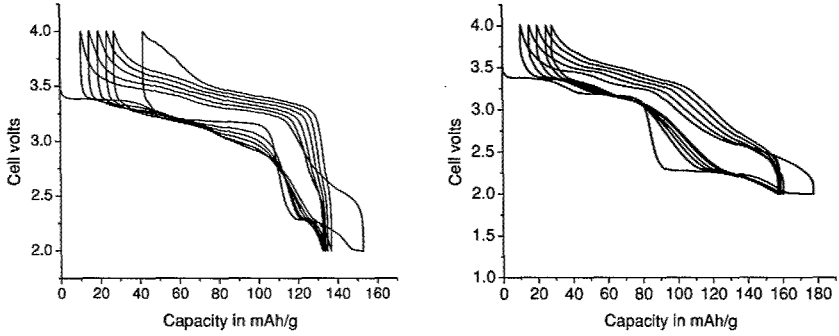

Figure 4. Electrochemical cycling of the vanadium oxide fibers in the $LiAsF_6$ based electrolyte of (left) the hydrothermal product and (right) after heating in oxygen.

Comparison of the electrochemical behavior of V_2O_5 fibers formed by heating the hydrothermal product in oxygen to pure V_2O_5 from Aldrich reveals the effect of particle size and morphology on redox performance of V_2O_5. The fibrous nano V_2O_5 shows a better redox behavior than the bulk V_2O_5; this may be associated with the much smaller distances that the Li^+ ion must diffuse in V_2O_5 fiber as the fiber is only 30 nm compared to the 60 μm of bulk V_2O_5. This observation has also been reported elsewhere with V_2O_5 cathodes [13]. The data shows that it is possible to use the template method to prepare nanostructured electrodes with improved capacity and cyclability. A challenge that remains is to develop a method for mass production of such materials.

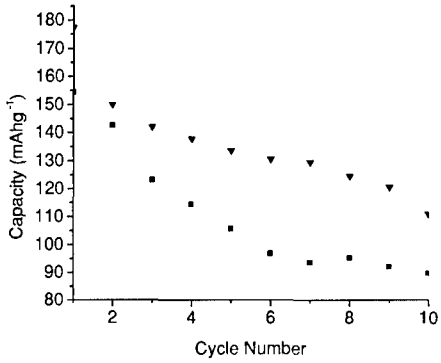

Figure 5. Electrochemical cycling of the hydrothermal product in $LiAsF_6$ salt before (■) and V_2O_5 fibers (▼) in $LiAsF_6$ salt

CONCLUSIONS

For the first time nanostructured vanadium oxides have been synthesized using organic polymer as template .We have also shown that the morphology of vanadium oxides can be preserved at temperature above 300 °C and 500 °C in oxygen and nitrogen respectively. Electrochemical studies of these compounds in lithium cell shows that they are redox active for lithium insertion.

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References:

1. C.R. Walk in *Lithium Batteries*, Academic Press, NewYork (1983).
2. M.S. Whittingham, *J. Electrochem. Soc.* **123**, 315-320 (1976).
3. B.E. Koene, N.J. Taylor, and L.F. Nazar, *Angew. Chem. Int. Ed.* **19**, 2888 (1999).
4. G.R Patzke, F. Krumeich, and R. Nesper, *Angew. Chem. Int. Ed.* **41**, 2446 (2002).
5. P.M. Ajayan, O. Stephan, P. Redlich, and C. Colliex, *Nature*. **375**, 564 (1995).
6. F. Krumeich, H. J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, and R. Nesper, *J. Am. Chem. Soc.* **121**, 8324 (1999).
7. X. Wang, L.Liu, R.Bontchev, and A. J. Jacobson, *Chem. Commun.* 1009-1010 (1998)
8. C.Boswell, *Chemical Market Reporter*.**268**, No8, August20-27, 2001
9. A.G. MacDiarmid, W.E. Jones, Jr, I.D. Norris, J.Gao, A.T. Johnson, Jr., N.J. Pinto, J. Hone, B. Han, F.K. Ko, H. Okuzaki, and M. Liaguno, *Synthetic Metals*. **119,** 27 (2001).
10. K. Ngala, J. Schutle, P.Y. Zavalij, and M.S. Whittingham, To be published.
11. T. Yao, Y. Oka, N. Yamamoto, *Mater. Res. Bull.* **27**, 669 (1992).
12. F. Zhang, P.Y. Zavalij, and M.S. Whittingham, *Mater. Res. Bull.* **32**, 701 (1997).
13. C.J. Patrissi and C.R. Martin, *J. Electrochem. Soc.* **148,** A1247, (2001).